COATINGS. ENAMELS

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INSULATING ENAMELS WITH IMPROVED DIELECTRIC PROPERTIES

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The effect of the content of alkali oxides on the physicomechanical and dielectric properties of glasses of the $SiO_2 - B_2O_3 - R_2O - BaO$ system is studied. The optimum ratio of (Na + K) : Li providing for manifestation of the polyalkali effect at different concentrations of B_2O_3 is established. The considered compositions can be used as an insulating coating on ozonizer parts.

Dielectric coatings for steels and alloys used as parts of state-of-the-art electrotechnical equipment require in each case a specific combination of technological, electric, and service properties.

The following materials are currently used:

polyorganosiloxane coatings that exhibit high values of the thermal coefficient of linear expansion (TCLE) and decreased temperatures of protective-layer formation; however, in the course of thermal aging the protective coating becomes thinner and its insulating properties deteriorate;

ceramic coatings that have a high level of Tk-100 (the temperature at which the specific volume resistance is equal to 100 MΩ) but exhibit increased porosity and a low TCLE.

The above drawbacks can be overcome using vitreous coatings that combine high values of the TCLE with gas permeability and relatively low refractoriness, although some researchers report on lower insulating parameters for these coatings as compared to ceramic materials.

The areas of practical application of vitreous enamels are restricted either by their insufficiently high insulating properties (which is typical of alkali compositions) or by increased refractoriness and a low TCLE (for alkali-free compositions).

There is currently a demand for fusible insulating enamels for steel. In particular, they are used as an insulating coating for components of ozonizers [1, 2], whose use will make it possible to replace chlorination of drinking water, paper pulp, etc. by environmentally safe ozonization.

The main difficulty in solving this problem consists in the fact that the compounds traditionally used to increase the TCLE contain cations of alkali metals, which are electric-current carriers and sharply decrease the electrical resistance of enamels.

The present study investigated the problem of using vitreous enamels as a coating of ozonizer electrodes made of stainless steel.

The problem of synthesis consists in the need to attain high values of Tk-100 and a matched TCLE. At the same time, in order to increase the output of ozone, the tangent of the dielectric-loss angle should not exceed 0.01, and the dielectric permittivity should be at least 5.

For the solution of this problem, vitreous materials of the $SiO_2 - B_2O_3 - R_2O - BaO$ system with slight additives of CaO, SrO, CdO, CoO, NiO, and MnO were obtained (R_2O is $Li_2O + Na_2O + K_2O$, the overall content of R_2O comprises 15%).

The glass considered had good melting qualities and melted completely at a low temperature (1250°C), and no extraneous inclusions or bubbles were identified.

As was noted, the low temperature of synthesis is related to the presence of alkali oxides in the compositions considered, which are modifiers and have a liquefying effect on the glass melt, i.e., act as fluxes.

The ratio $(Li^+ + Na^+) : K^+$ is taken as the criterion characterizing the dependence of the properties on the enamel composition. Moreover, all considered samples were divided into three series depending on the ratio $Li_2O : R_2O$.

To study the effect of different ratios of alkali oxides on the physicochemical properties of the synthesized glasses, the following properties were determined: volume mass ρ, microhardness H, TCLE α, deformation start temperature

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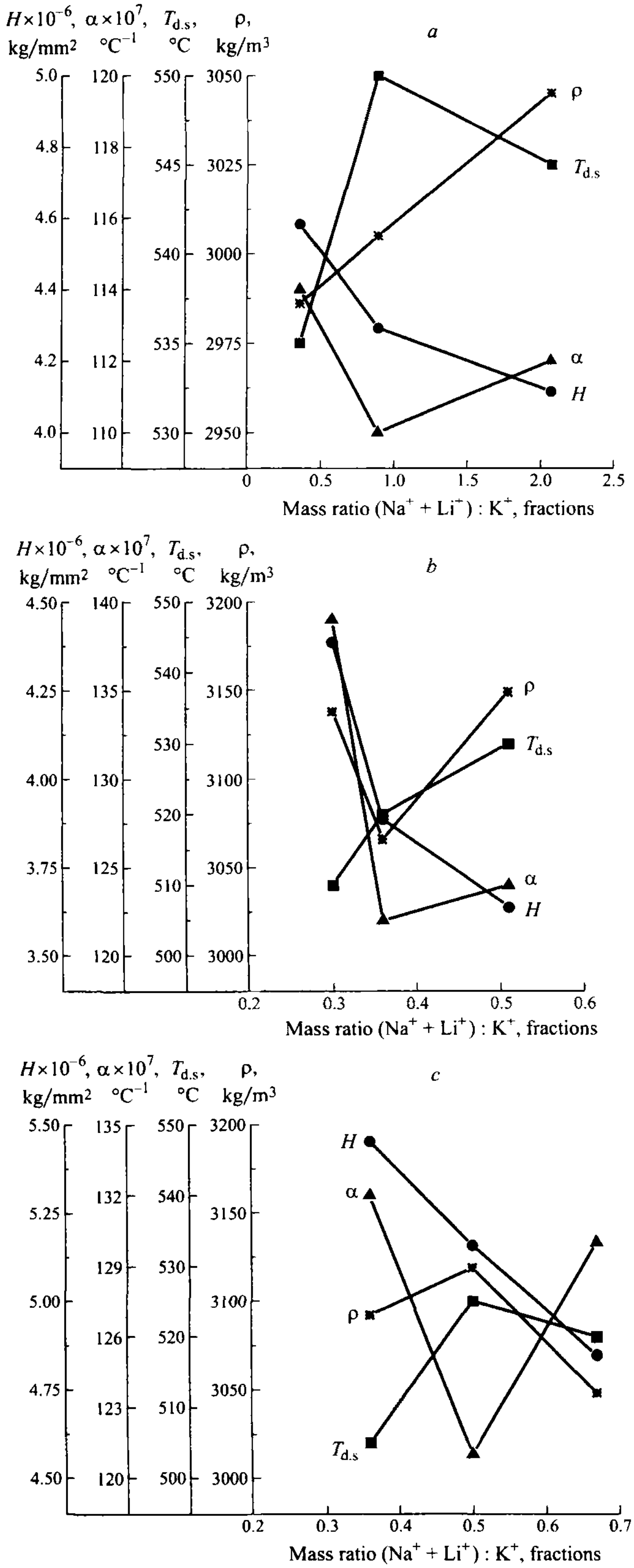

Fig. 1. Variation of the physicomechanical properties of glass depending on its composition: *a*) $Li_2O : R_2O = 0.03$; *b*) $Li_2O : R_2O = 0.11$; *c*) $Li_2O : R_2O = 0.15$.

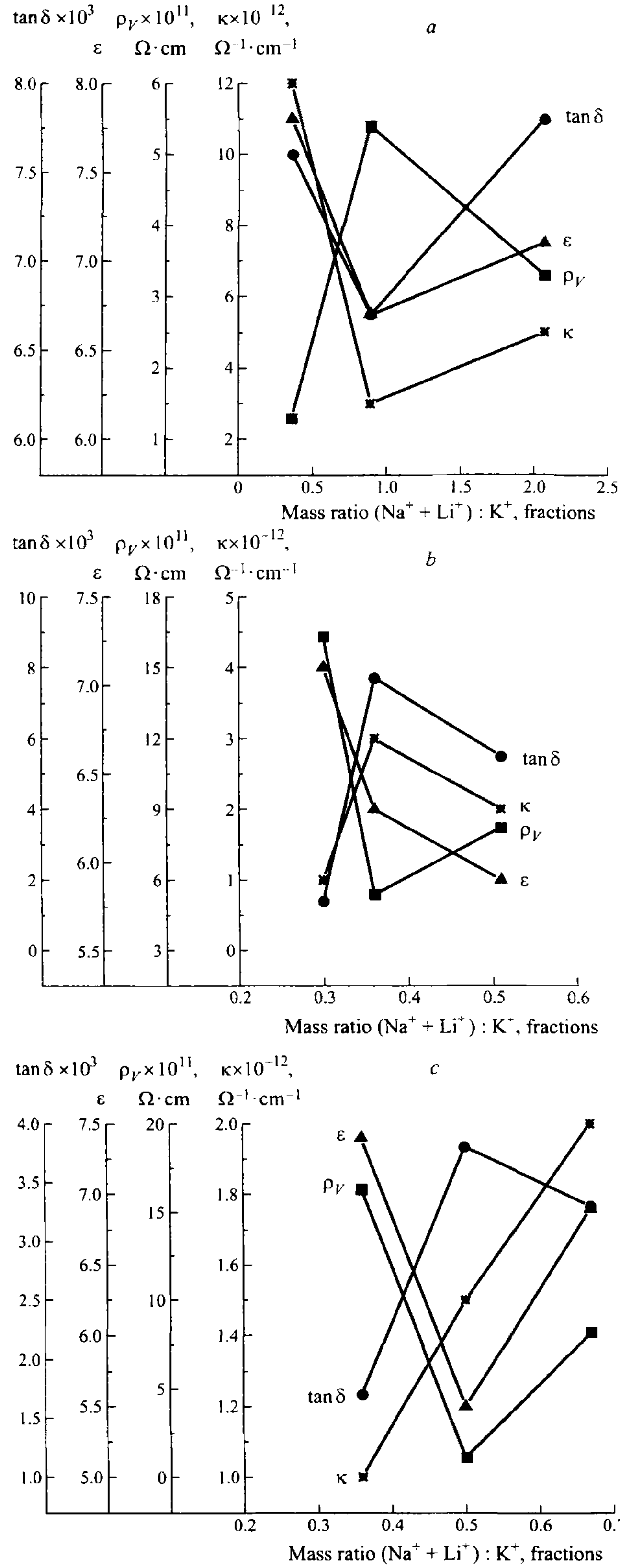

Fig. 2. Variation of the dielectric properties of glass depending on its composition: *a*) $Li_2O : R_2O = 0.03$; *b*) $Li_2O : R_2O = 0.11$; *c*) $Li_2O : R_2O = 0.15$.

$T_{d.s}$, tangent of the dielectric-loss angle $\tan\delta$, dielectric permittivity ε, specific conductivity κ, volume electrical resistance ρ_V. The data obtained are shown in Figs. 1 and 2.

It can be seen that the volume mass of the glasses depends to a great extent on the ratio of the alkali elements.

This can probably be accounted for by the fact that variations of the ratios between the lighter Li^+ and Na^+ ions, which have a small radius, and the K^+ ions, which are larger in size and mass, result in different filling of cavities in the silicon carbide skeleton. Accordingly, the amount of mass per unit volume will vary, i.e., the optimum filling of the structure corresponds to the maximum value of the density.

With increase in the ratio $(Na^+ + Li^+) : K^+$, the microhardness decreases, i.e., when K^+ is replaced by Na^+, the structure becomes less strong.

Analysis of the data obtained in a study of the thermal properties indicates that when K_2O is replaced by Na_2O, the TCLE decreases, since a decrease in the content of K^+ ions in the sample increases the filling of the structure with Na^+ ions and the degree of adhesion of the silicon-oxygen skeleton.

In considering the results of calculating $T_{d.s}$, no obvious dependence of $T_{d.s}$ on the composition of the glass can be identified, since all the data are rather close to each other and are within the same temperature region.

Moreover, dependences of the dielectric permittivity on the ratio $(Li^+ + Na^+) : K^+$ were revealed (see Fig. 2). As the Na content in the glass composition increases, the value of ε decreases, since the amount of the smaller and less polarized Na^+ ions increases. The appearance of deflections on the graph can be ignored, since these deviations are within the limits of the measurement error [3].

The dependence of $\tan\delta$ for compositions with a ratio of $Li_2O : R_2O_3 = 0.03$ (see Fig. 2*a*) does not exhibit marked variations of the values over the sample series. The high values of $\tan\delta$ can be accounted for by a higher content of Na^+ as compared to the two other sample series. These high values are inadmissible for enamels intended for a coating of ozonizer electrodes.

In compositions with a ratio of $Li_2O_3 : R_2O$ equal to 0.11 and 0.15 (see Fig. 2*b* and *c*) the polyalkali effect is manifested in the decrease in $\tan\delta$. This is an indication of the optimum composition of the enamel and the optimum ratio of the oxides that caused the polyalkali effect.

The glasses considered contain oxides of three alkali metals that have a basic effect on the specific conductivity and the volume electrical resistance. In glasses with a ratio of $Li_2O : R_2O$ equal to 0.03 a maximum on the curve of ρ_V and a minimum on the curve of κ were recorded.

When the ratio of $Li_2O : R_2O$ is equal to 0.11 and 0.15, the polyalkali effect is manifested in decreased conductivity and, accordingly, an increased resistance of samples in which the ratio of the alkali oxides proved to be optimum for manifestation of that effect.

Thus, the polyalkali effect in boron-silicate glasses containing up to 15 wt.% B_2O_3 is observed at a ratio of $(Na^+ + K^+) : Li^+$ approximately equal to 1. In similar glasses containing up to 10% B_2O, the polyalkali effect is observed at a ratio of $(Na^+ + K^+) : Li^+$ equal to 0.4 – 0.5.

Thus, by varying the content of the oxides within the indicated limits, the dielectric properties of enamels based on the $SiO_2 - B_2O_3 - R_2O - BaO$ system can be controlled. This does not change the temperature of their adhesion on metal and other technological parameters.

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